Electronic Supplementary Information

for

Electron-Transporting Polymers Based on Double B←N

Bridged Bipyridine (BNBP) Unit

Xiaojing Long,[a,b] Yao Gao,[a,b] Hongkun Tian,[a] Chuandong Dou,[a]* Donghang Yan,[a] Yanhou Geng,[c] Jun Liu,[a]* and Lixiang Wang[a]

[a]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China*
[b]*University of Chinese Academy of Sciences, Beijing 100039, P. R. China*
[c]*School of Material Science and Engineering and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, P. R. China*
Email: chuandong.dou@ciac.ac.cn, liujun@ciac.ac.cn

Contents

1. Experimental details

General. ^{1}H NMR spectra were measured with a Bruker AV-400 (400 MHz) spectrometer in $C_6D_4Cl_2$ at 100 °C or C_6D_6 at 25 °C. Chemical shift is reported in δ ppm using $C_6H_4Cl_2$ (7.29 ppm) or C_6H_6 (7.16 ppm) for ^{1}H NMR. Elemental analysis was performed on a VarioEL elemental analyzer. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) on a PL-GPC 220-type at the temperature of 150 °C. 1,2,4-Trichlorobenzene (TCB) was used as the eluent and monodisperse polystyrene was used as the standard. UV/Vis absorption spectra were measured with a Shimadzu UV-3600 spectrometer in spectral grade solvents. Thermal gravimetric analysis (TGA) was performed under an N_2 flow with a Perkin-Elmer-TGA 7 system. The temperature of degradation (T_d) was corresponding to a 5% weight loss. The differential scan calorimetry (DSC) was performed on a TA Instruments Q2000 DSC. Both the heating and the cooling rates were set to 10 °C min^{-1}. Atomic force microscopy (AFM) was performed with a SPA300HV (Seiko Instruments, Inc., Japan) in tapping mode. GIXRD data was obtained on a Bruker D8 Discover reflector (Cu Kα, λ = 1.54056 Å) under 40 kV and 40 mA tube current. The scanning speed is 3 s per step with 0.1° step size (2θ). The measurement was obtained in a scanning interval of 2θ between 2° and 30°. The in-plane X-ray diffraction (IPXRD) profiles were obtained using a Rigaku SmartLab with an X-ray generation power of 40 kV tube voltage and 30 mA tube current. The diffraction was recorded in the $2\theta-\chi$ mode. The scanning speed is 5 s per step with 0.02° step size (2θ). The measurement was obtained in a scanning interval of 2θ between 2° and 30°. Cyclic voltammetry (CV) was performed on an CHI660a electrochemical workstation using n-Bu$_4$NClO$_4$ (0.1 M) in acetonitrile as electrolyte solution and ferrocene as an internal reference at a scan rate of 100 mV s^{-1}. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a standard calomel reference electrode. The polymer was spin-casted on the working electrode for measurements. The redox potentials were calibrated with ferrocene as an internal standard. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equations: $E_{\text{HOMO/LUMO}}$ = $-$(4.80 + $E_{\text{onset}}^{\text{ox}}/E_{\text{onset}}^{\text{red}}$) eV. All reactions were performed under argon atmosphere.

Materials and reagents. All solvents were distilled via standard method. The compounds 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethane, 5,5'-bis(trimethylstannyl)-3,3'-difluoro-2,2'-bithiophene were prepared according to references.[1] Other reagents were used as purchased unless stated.

Synthesis and Characterization.
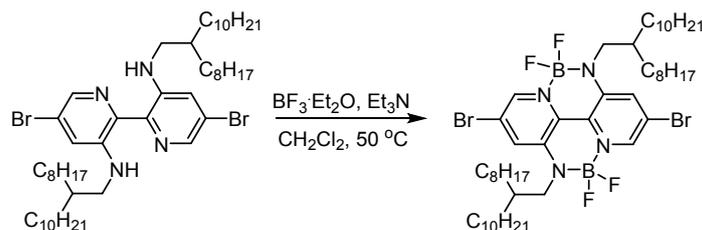
BNBP monomer: The BNBP monomer was prepared according to reference.[2] ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 8.22 (d, J = 1.6 Hz, 1H), 7.28 (d, J = 1.6 Hz, 1H), 3.41 (d, J = 6.8 Hz, 2H), 1.78 (s, 1H), 1.39–1.28 (m, 32H), 0.94–0.90 (m, 6H). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 144.69, 128.56, 125.64, 125.37, 122.28, 48.63, 36.02, 32.37, 32.34, 32.15, 30.52, 30.50, 30.14, 30.07, 29.86, 29.79, 26.87, 23.16, 23.14, 14.41. ^{11}B NMR (128 MHz, C$_6$D$_6$, 25 °C): δ (vs. BF$_3$·Et$_2$O) 1.0. ^{19}F NMR (376 MHz, C$_6$D$_6$, 25 °C): δ (vs. fluorobenzene) −30.77. Anal. Calcd for C$_{50}$H$_{86}$B$_2$Br$_2$F$_4$N$_4$: C, 60.01; H, 8.66; B, 2.16; Br, 15.97; F, 7.59; N, 5.60. Found: C, 60.13; H, 8.48; N, 5.48.

P-BNBP-TVT: Starting materials of the BNBP monomer (170 mg, 0.17 mmol), the 1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (88 mg, 0.17 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (3.5 mg, 0.0034 mmol), and P(o-Tolyl)$_3$ (8.3 mg, 0.027mmol) were placed in a two-necked flask under argon, and then dried toluene (45 mL) was added. After the mixture being stirred at 120 °C for 24 h, end-capping reaction was carried out by adding 1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (7.16 mg, 0.0136 mmol) and then bromobenzene (200 mg, 1.28 mmol). After cooling, the resulting organic phase was extracted with chlorobenzene (150 mL) and washed with water. After the solvents being removed, the residue was dispersed in acetonitrile and the precipitate was collected. The polymer was purified by Soxhlet extraction with acetone, hexane, and THF to remove impurities and catalysts as well as the residual monomers. The left residual was finally dissolved in hot o-DCB, which was then dispersed in acetonitrile. The polymer **P-BNBP-TVT** was collected and dried in vacuum overnight. Yield: 166 mg (95%). ^{1}H NMR (400 MHz, C$_6$D$_4$Cl$_2$, 100 °C): δ 8.68 (s, 1H), 7.93 (s, 2H), 3.94 (s, 2H), 2.27 (s, 1H), 1.75–1.35 (m, 32H), 1.08 (s, 6H). The polymer has formed some aggregation in the hot solution, resulting in more proton signals of alkyl chains. GPC (TCB, polystyrene standard, 150 °C): M_n = 41.6 kDa, PDI = 4.3. Anal. Calcd for C$_{60}$H$_{92}$B$_2$F$_4$N$_4$S$_2$: C, 69.89; H, 8.99; B, 2.1; F, 7.37; N, 5.43; S, 6.22. Found: C, 69.69; H, 8.81; N, 5.62; S, 6.35.

P-BNBP-BT: **P-BNBP-BT** was synthesized from the BNBP monomer and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene following the procedure for the synthesis of **P-BNBP-TVT.** Yield: 184 mg (95%). ^{1}H NMR (400 MHz, $C_6D_4Cl_2$, 100 °C): δ 8.70 (s, 1H), 7.95 (s, 1H), 7.56 (s, 1H), 3.96 (s, 2H), 2.29 (s, 1H), 1.80–1.34 (m, 32H), 1.08 (s, 6H). The polymer has formed some aggregation in the hot solution, resulting in more proton signals of alkyl chains. GPC (TCB, polystyrene standard, 150 °C): M_n = 42kDa, PDI =1.67. Anal. Calcd for $C_{58}H_{90}B_2F_4N_4S_2$: C, 69.31; H, 9.03; B, 2.15; F, 7.56; N, 5.57; S, 6.38. Found: C, 69.08; H, 8.89; N, 5.68; S, 6.26.

P-BNBP-fBT: **P-BNBP-fBT** was synthesized from BNBP monomer and 5,5'-bis(trimethylstannyl)-3,3'-difluoro-2,2'-bithiophene following the procedure for the synthesis of **P-BNBP-TVT**, which was reported in our previous work. Yield: 137 mg (97%). ^{1}H NMR (400 MHz, $C_6D_4Cl_2$, 100 °C): δ 8.64 (s, 1H), 7.91 (s, 1H), 3.95 (s, 2H), 2.26 (s, 1H), 1.78–1.34 (m, 32H), 1.08 (s, 6H). GPC (TCB, polystyrene standard, 150 °C): M_n = 116.0 kDa, PDI = 2.6. Anal. Calcd for $C_{58}H_{88}B_2F_6N_4S_2$: C, 66.91; H, 8.52; B, 2.08; F, 10.95; N, 5.38; S, 6.16. Found: C, 67.01; H, 8.51; N, 5.33; S, 6.22.

2. Thermal properties

The thermal properties of **P-BNBP-TVT**, **P-BNBP-BT** and **P-BNBP-fBT** were determined by thermogravimetric analysis (TGA) and differential scan calorimetry (DSC). TGA analysis shows that they have good thermal stability with decomposition temperature (T_d) at 5% weight loss of 412 °C for **P-BNBP-TVT**, 363 °C for **P-BNBP-BT** and 370 °C for **P-BNBP-fBT** under N_2, respectively.
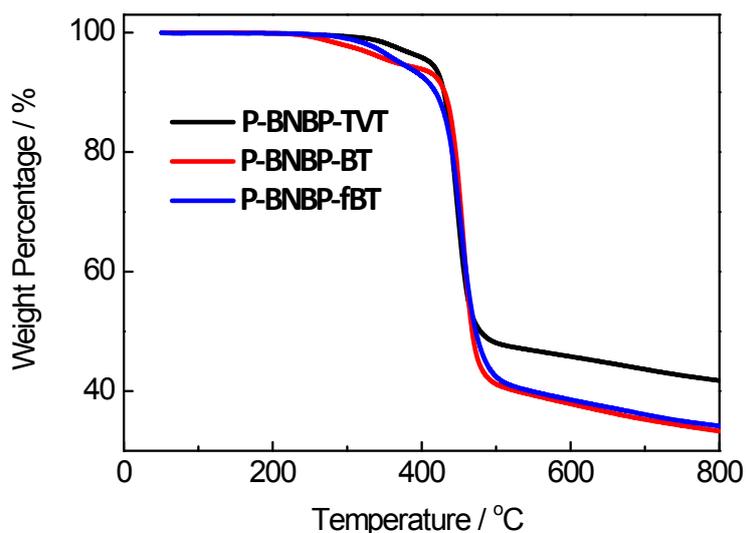
Figure S1. TGA curves of **P-BNBP-TVT, P-BNBP-BT** and **P-BNBP-fBT**.
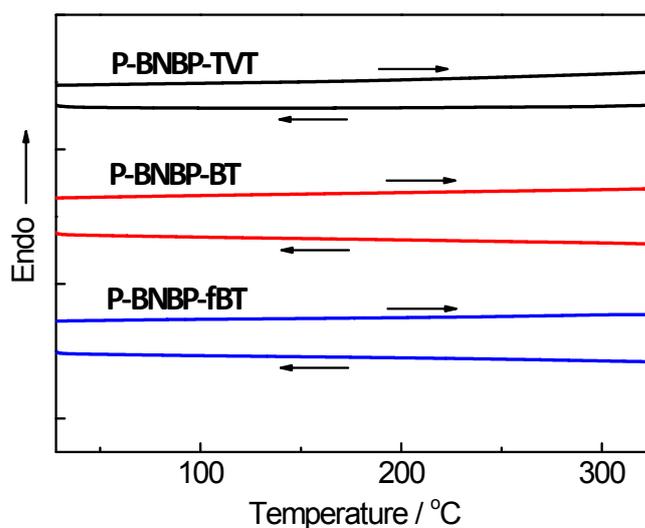
Figure S2. DSC curves of **P-BNBP-TVT, P-BNBP-BT** and **P-BNBP-fBT**, including first cooling and second heating scans.

5

3. Photophysical properties
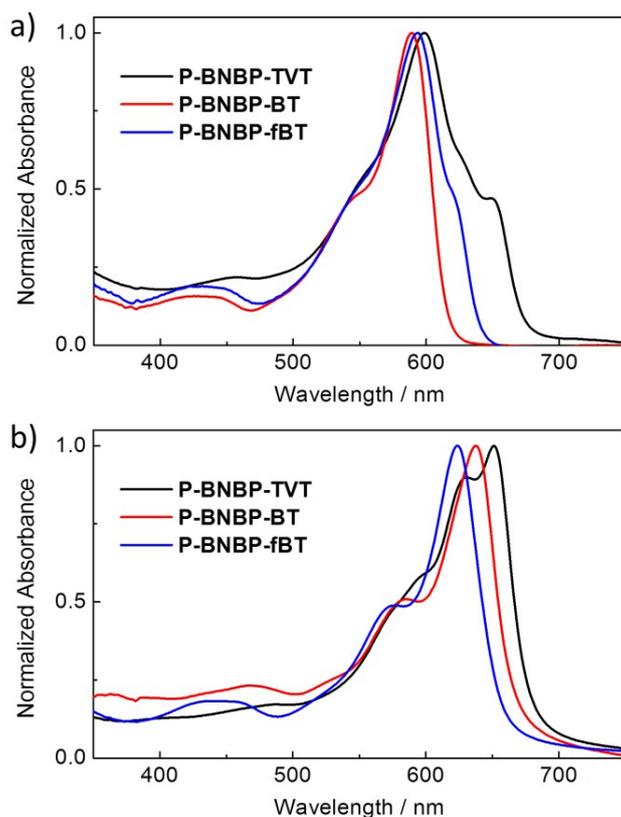
Figure S3. UV/Vis absorption spectra of **P-BNBP-TVT**, **P-BNBP-BT** and **P-BNBP-fBT** a) in *o*-DCB solutions at 100 °C and b) in thin films.
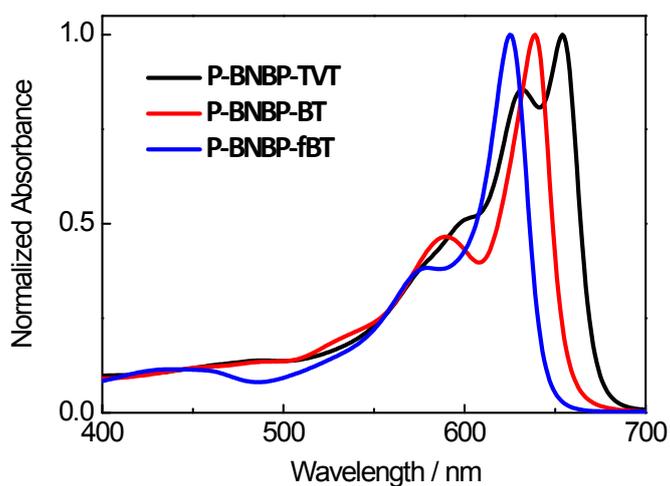
Figure S4. UV/Vis absorption spectra of **P-BNBP-TVT**, **P-BNBP-BT** and **P-BNBP-fBT** in *o*-DCB solutions at 25 °C. In comparision to that of the polymers in *o*-DCB solutions at 100 °C, there have been some aggregates in the *o*-DCB solutions at 25 °C.
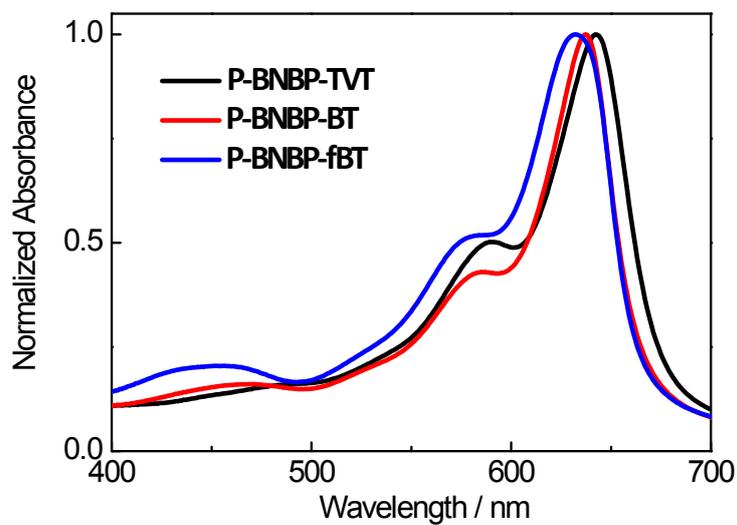
Figure S5. UV/Vis absorption spectra of the films annealed at 200 °C of **P-BNBP-TVT**, **P-BNBP-BT** and **P-BNBP-fBT**. After annealing at 200 °C, the absorption peak of the **P-BNBP-TVT** film is blue-shifted by 8 nm.
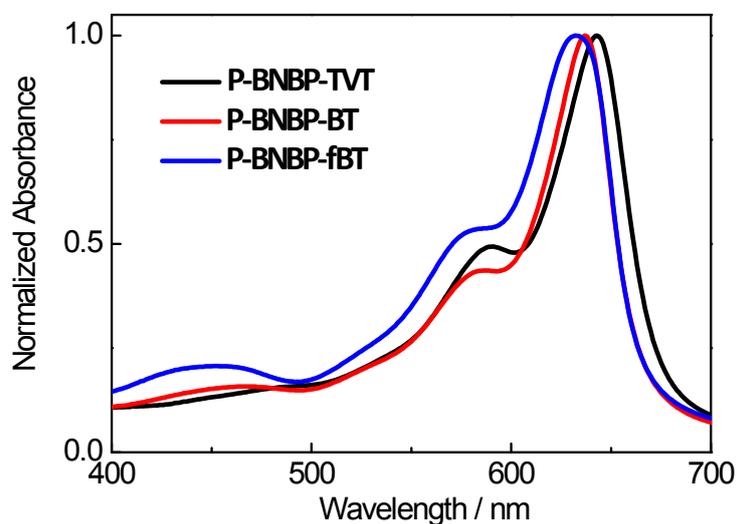
Figure S6. UV/Vis absorption spectra of the films annealed at 250 °C of **P-BNBP-TVT**, **P-BNBP-BT** and **P-BNBP-fBT**. After annealing at 250 °C, the absorption peak of the **P-BNBP-TVT** film is blue-shifted by 8 nm.

4. Geometry optimizations and molecular orbitals

All calculations were performed with the Gaussian 09 program.[3] The geometry optimizations of the repeating units and the model compounds containing four repeating units with the long alkyl chains replaced by the methyl groups were performed using Gaussian 09 program at the B3LYP/6-31G* level of theory. The Kohn-Sham molecular orbitals of the model compounds were calculated at the same level of theory.
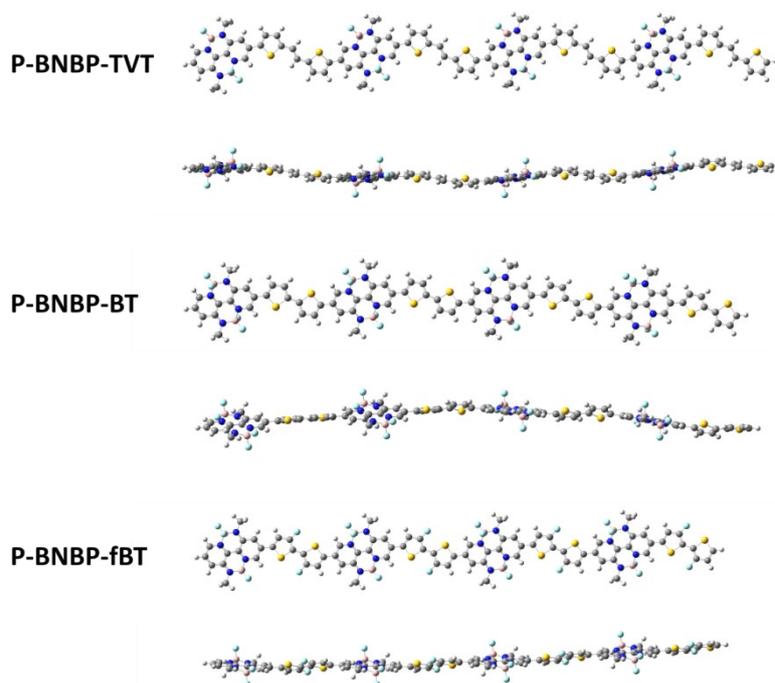
Figure S7. The optimized conformation of the model compounds of **P-BNBP-TVT**, **P-BNBP-BT** and **P-BNBP-fBT**.
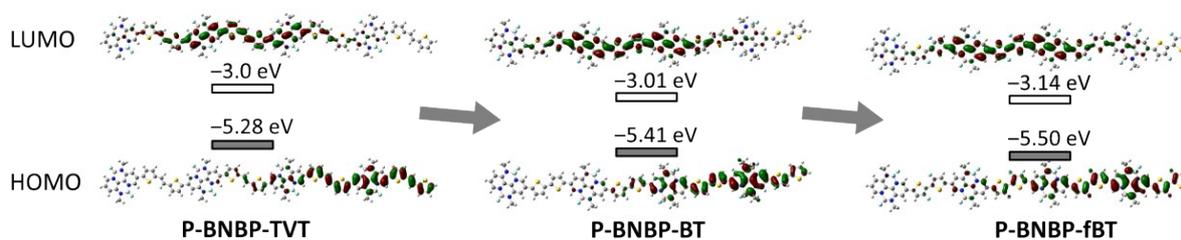
Figure S8. Kohn-Sham LUMOs and HOMOs of the model compounds of **P-BNBP-TVT**, **P-BNBP-BT** and **P-BNBP-fBT**, based on the calculations at the B3LYP/6-31G* level.

5. OTFT fabrications and characterizations

Top-gate/bottom-contact (TGBC) organic thin film transistors (OTFTs) were fabricated on silicon wafer covered with 300 nm SiO_2. The substrates were first cleaned with double-distilled water, acetone and isopropanol in an ultrasonic bath and then dried under a nitrogen flow. The substrates were heated at 120 °C for 5 min and finally treated through UV-zone instrument for 15 min. First, Au source/drain electrodes (~25 nm) were deposited on cleaned bare Si/SiO$_2$ wafer with W/L = 70 (W = 5.6 mm, L = 80 μm). The polymers in o-DCB solutions (2 mg/mL) were spin-casted on the substrates, followed by thermal annealing at 200 °C or 250 °C for 10 min. Then the solution of 80 mg/mL poly(methylmethacrylate) (PMMA) (product no. 182230 from Aldrich, Mw = 120 kDa) in butyl acetate (~550 nm) as dielectric was deposited by spin coating at 1200 rpm for 1 min and then annealed at 100 °C for 1 h. Finally, Au (~80 nm) was vacuum-deposited as gate electrode. Field-effect mobility was calculated in the saturation regime by using the equation: $I_D^{sat} = (\mu C_i W/2L)(V_G - V_T)^2$, where I_D is the drain-source current, μ is the field-effect mobility, C_i is the capacitance per unit area of the gate dielectric layer, V_G and V_T are the gate voltage and threshold voltage, respectively.
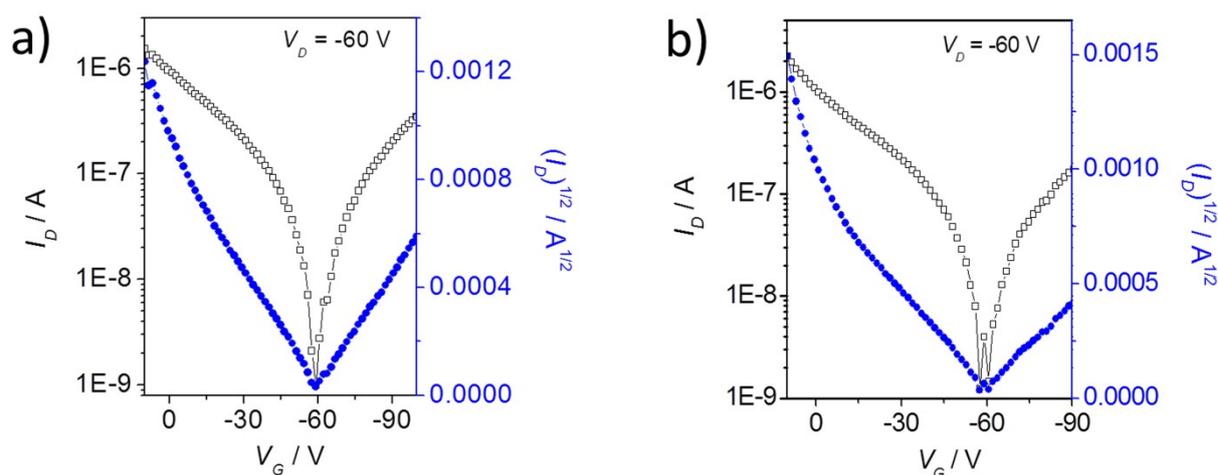
Figure S9. Transfer curves of OTFT devices with the **P-BNBP-BT** films annealed at a) 250 °C and b) 200 °C, respectively.
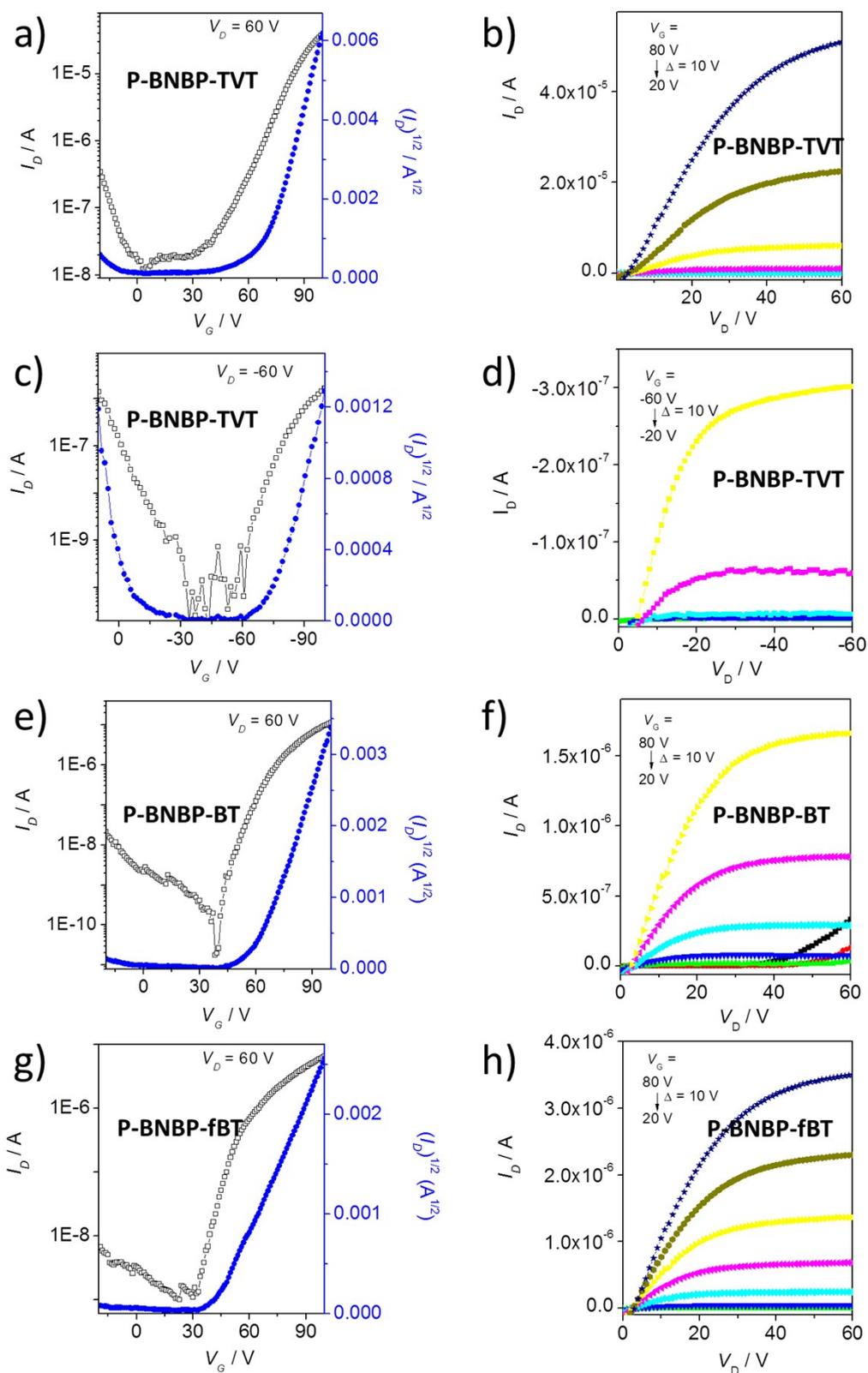
Figure S10. Transfer and output curves of OTFT devices with the polymer films annealed at 200 °C.

Table S1. OTFT device performance of the three polymer films.

Polymer	T_a[a] (°C)	p-channel				n-channel			
		$\mu_{h,max}$ (cm² v⁻¹ s⁻¹)	$\mu_{h,avg}$[b] (cm² v⁻¹ s⁻¹)	V_T[c] (V)	I_{on}/I_{off}[d]	$\mu_{e,max}$ (cm² v⁻¹ s⁻¹)	$\mu_{e,avg}$[b] (cm² v⁻¹ s⁻¹)	V_T[c] (V)	I_{on}/I_{off}[d]
P-BNBP-TVT	250	0.015	0.01	−60 to −70	10^5–10^6	0.32	0.25	55 to 65	10^5–10^7
	200	0.024	0.015	−59 to −70	10^4–10^5	0.21	0.15	38 to 46	10^4–10^5
P-BNBP-BT	250	1.4×10^{-3}	1.0×10^{-3}	−55 to −60	10^0–10^1	0.05	0.035	60 to 70	10^5–10^7
	200	9.0×10^{-4}	5.0×10^{-4}	−55 to −60	< 10	0.025	0.015	50 to 55	10^5–10^6
P-BNBP-fBT	250	–	–	–	–	0.02	0.015	45 to 50	10^4–10^5
	200	–	–	–	–	0.015	0.011	35 to 45	10^3–10^4

[a]Thermal annealing temperature. [b]The average values were calculated from four parallel devices in saturation region. [c]Threshold voltage. [d]Current on/off ratio.
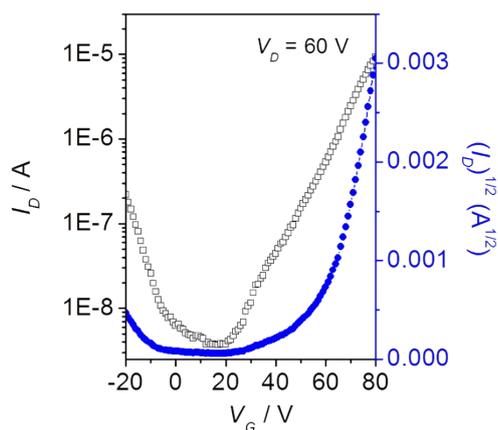
Figure S11. Transfer curves of **P-BNBP-TVT**-based OTFT device which was tested after stored in the air for 1 day. The used film was annealed at 250 °C. The μ_e decreases from 0.32 to 0.12 cm^2 V^{-1} s^{-1}.
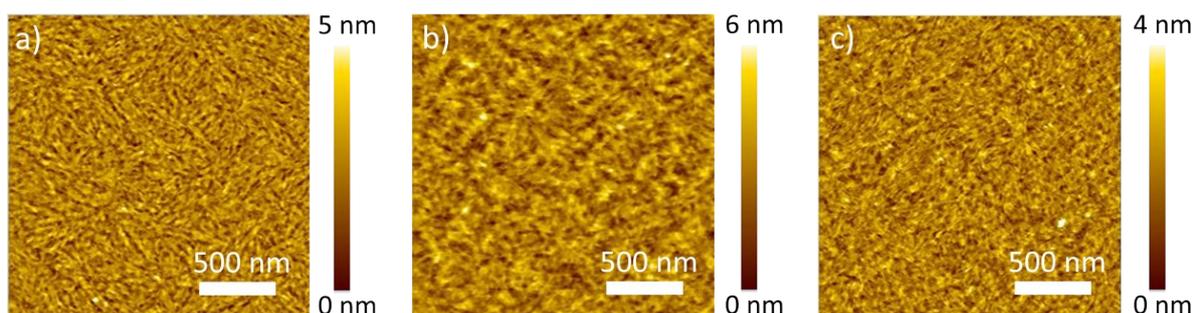
Figure S12. AFM height images of the thin films of a) **P-BNBP-TVT**, b) **P-BNBP-BT** and c) **P-BNBP-fBT** annealed at 250 °C, respectively.
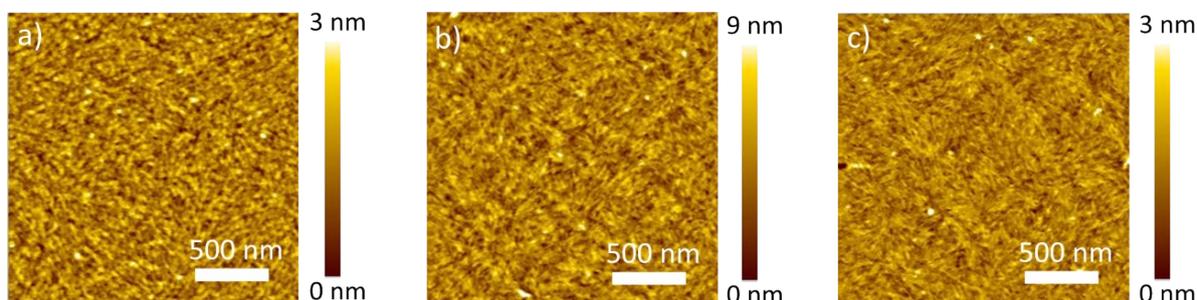
Figure S13. AFM height images of the thin films of a) **P-BNBP-TVT**, b) **P-BNBP-BT** and c) **P-BNBP-fBT** annealed at 200 °C, respectively.
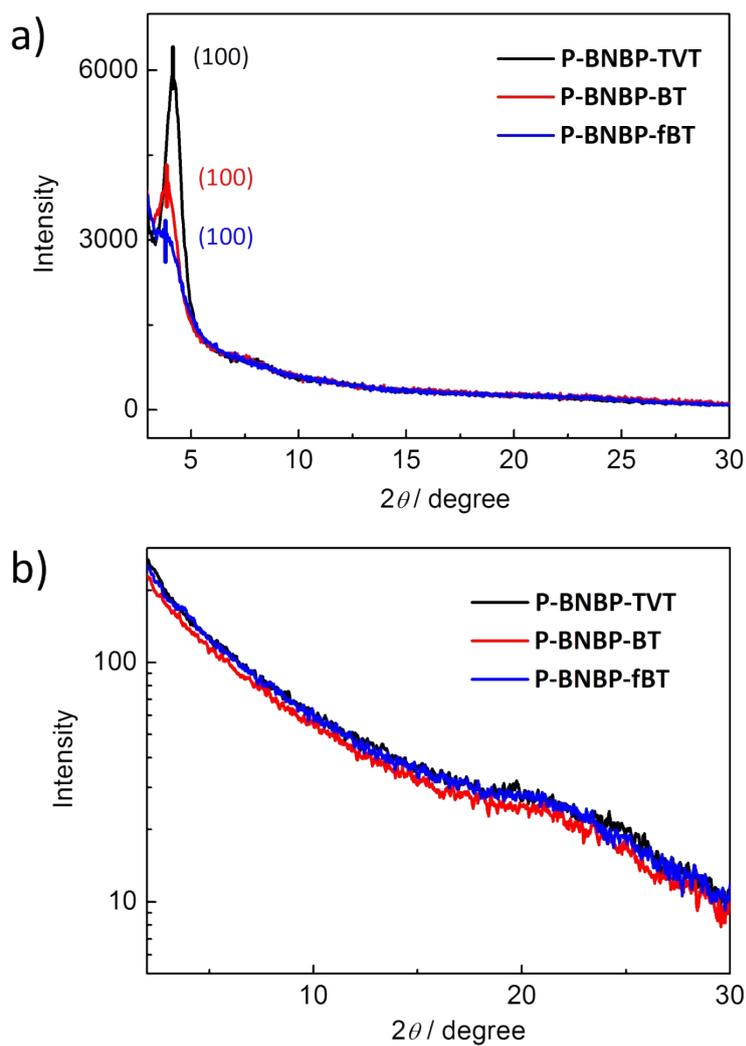
Figure S14. a) The GI-XRD patterns and b) the IP-XRD patterns of the three polymer films annealed at 200 °C, respectively. The weaker molecular packings of the three films annealed at 200 °C produced the lower OTFT performance compared with that of annealed at 250 °C.

13

6. References

(1) M. Nakano, I. Osaka and K. Takimiya, *Macromolecules,* 2015, **48**, 576.

(2) X. Long, Z. Ding, C. Dou, J. Zhang, J. Liu and L. Wang, *Adv. Mater.*, 2016, **28**, 6504.

(3) Gaussian 09 (Revision A.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian, Inc*., Wallingford CT, 2009.

7. ¹H NMR spectra
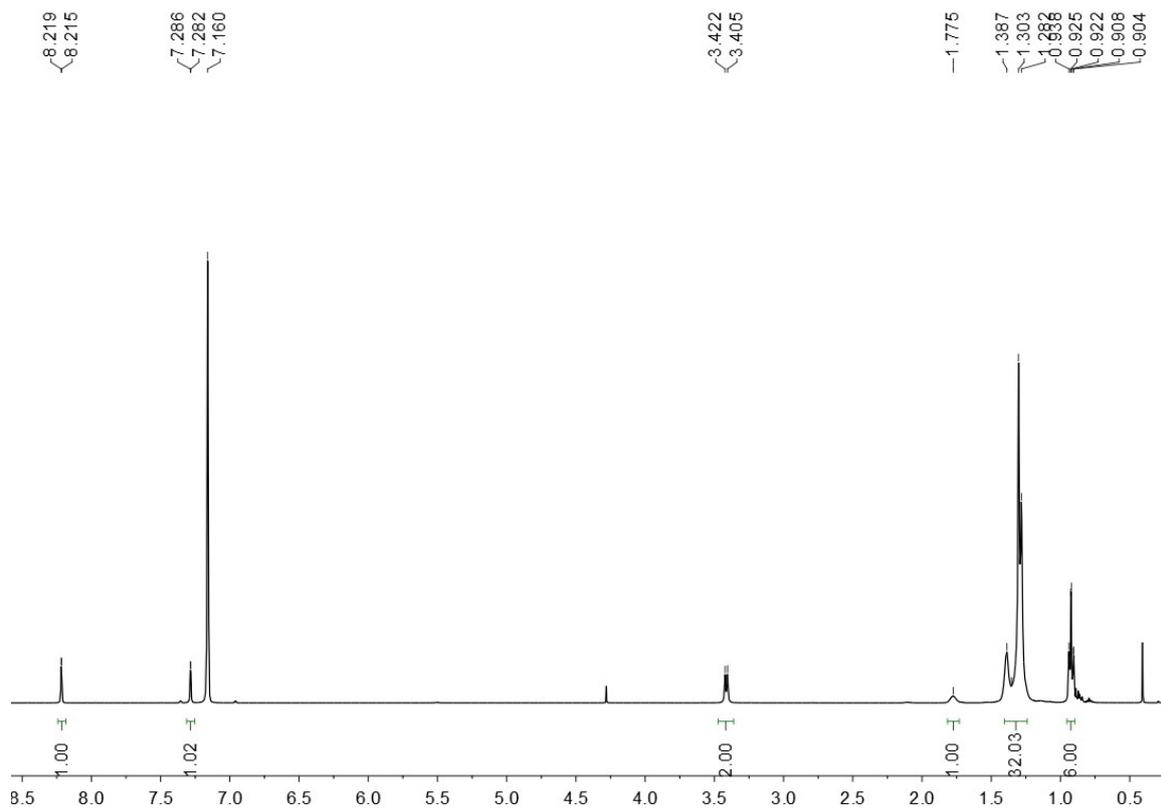
Figure S15. ¹H NMR spectrum of the BNBP monomer.
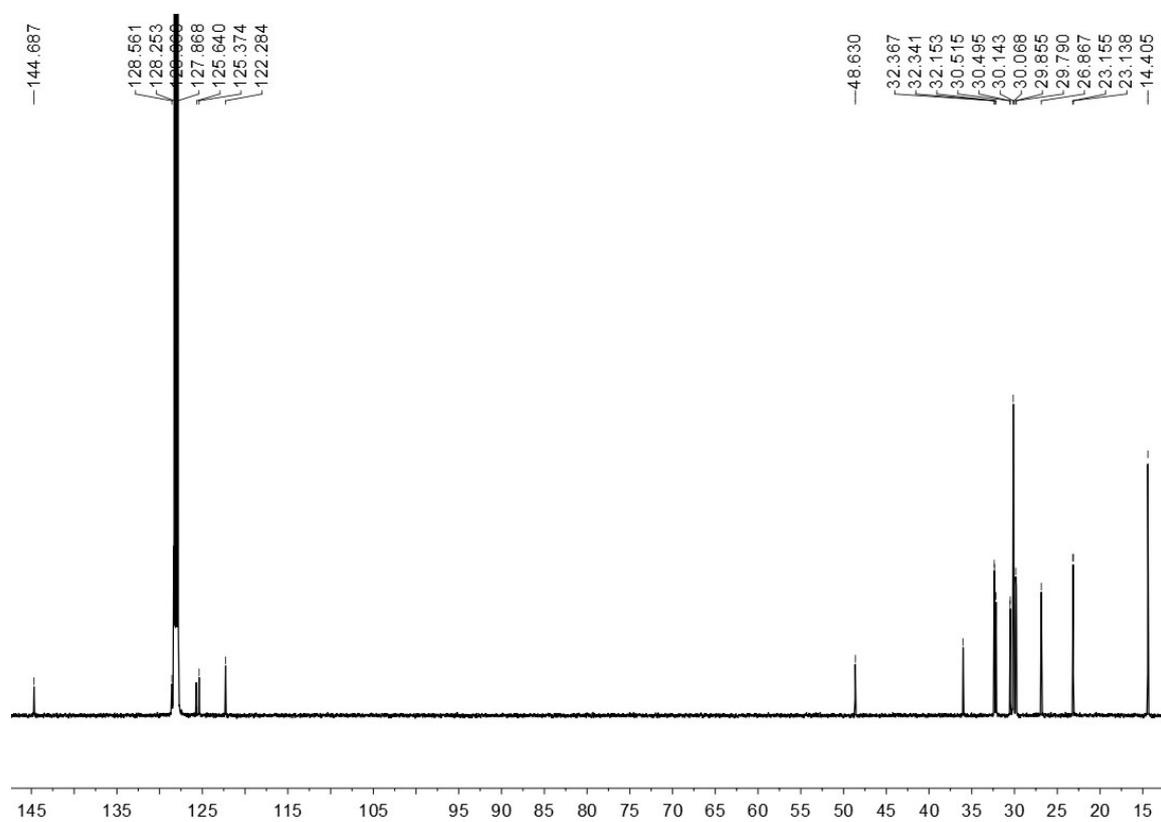
Figure S16. ¹³C NMR spectrum of the BNBP monomer.
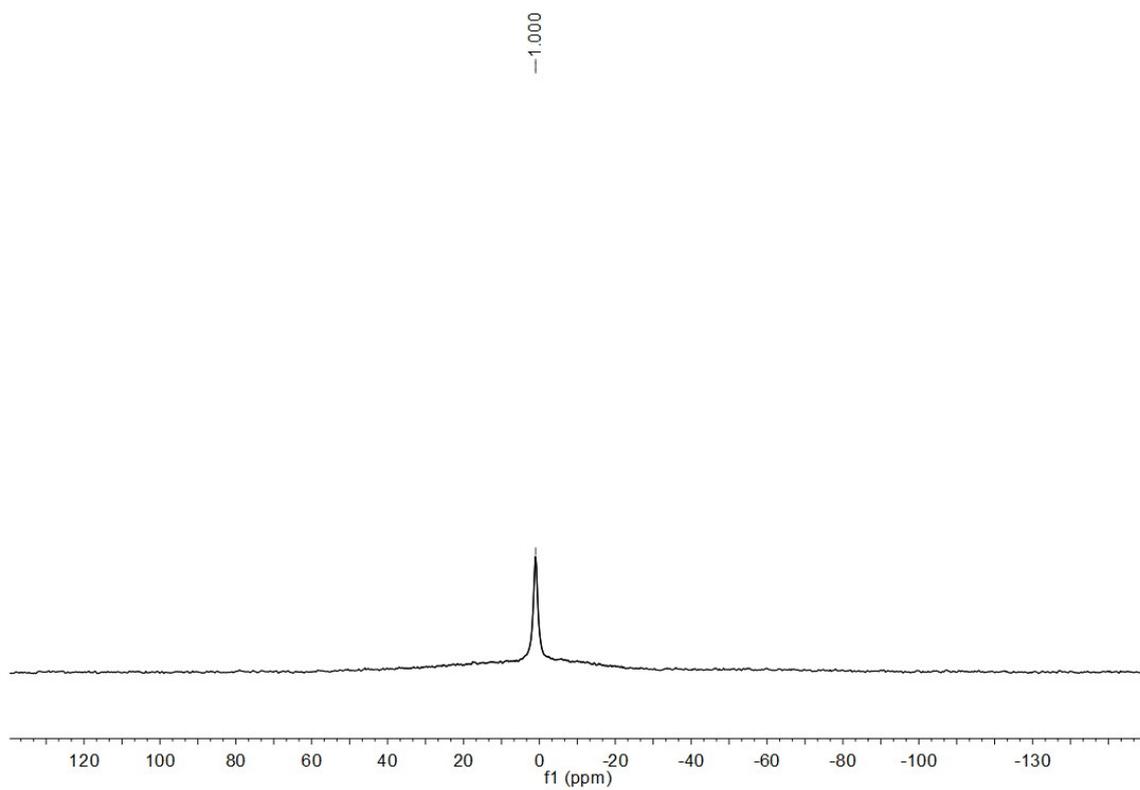
Figure S17. ¹¹B NMR spectrum of the BNBP monomer.
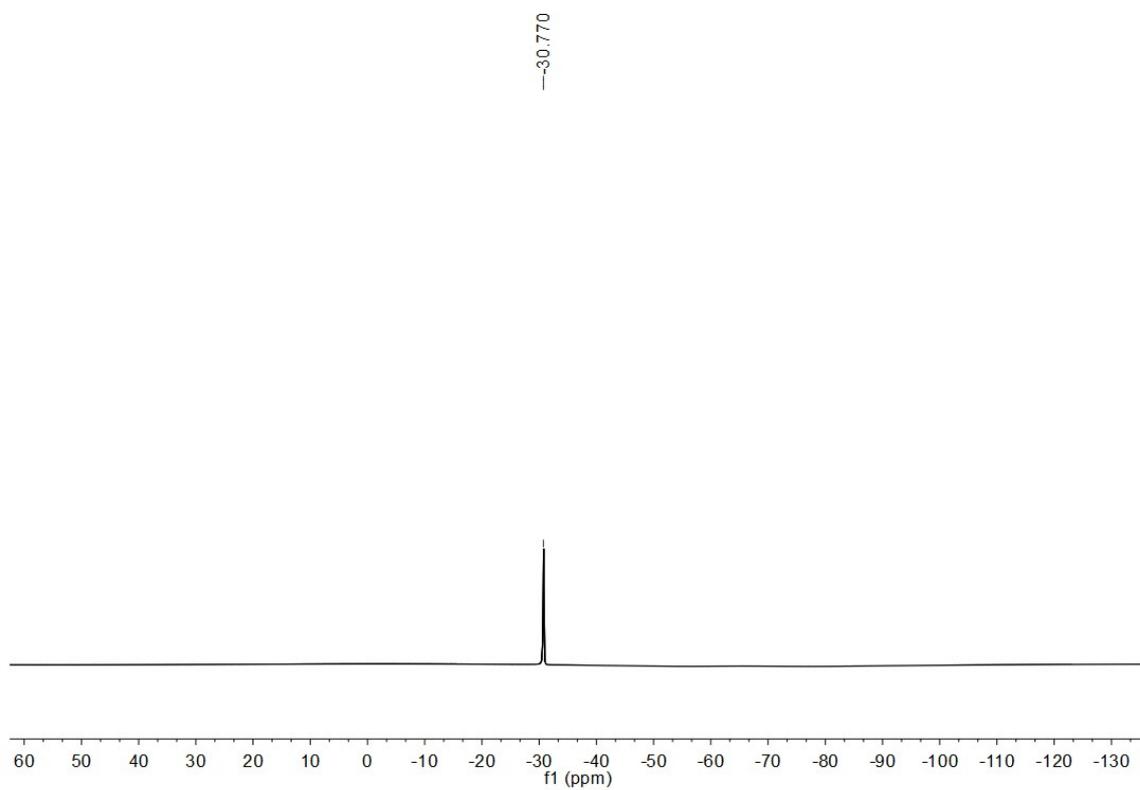
Figure S18. ¹⁹F NMR spectrum of the BNBP monomer.
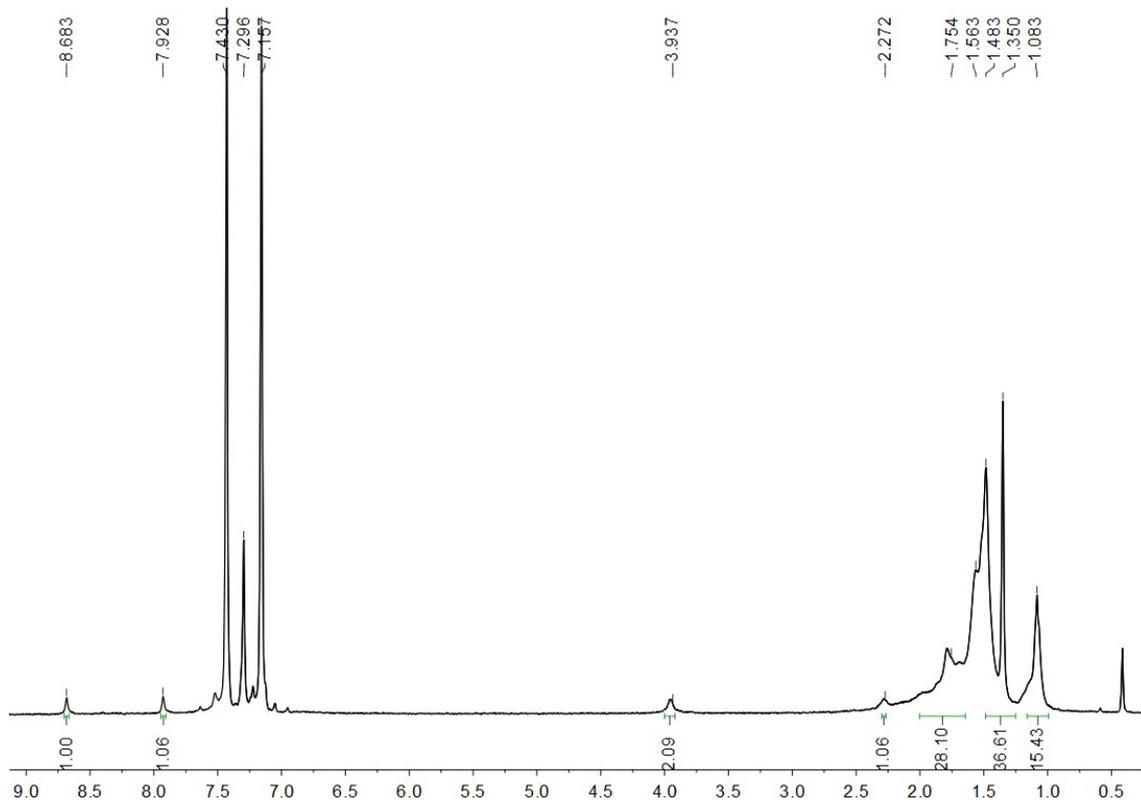
Figure S19. ^{1}H NMR spectrum of **P-BNBP-TVT**.
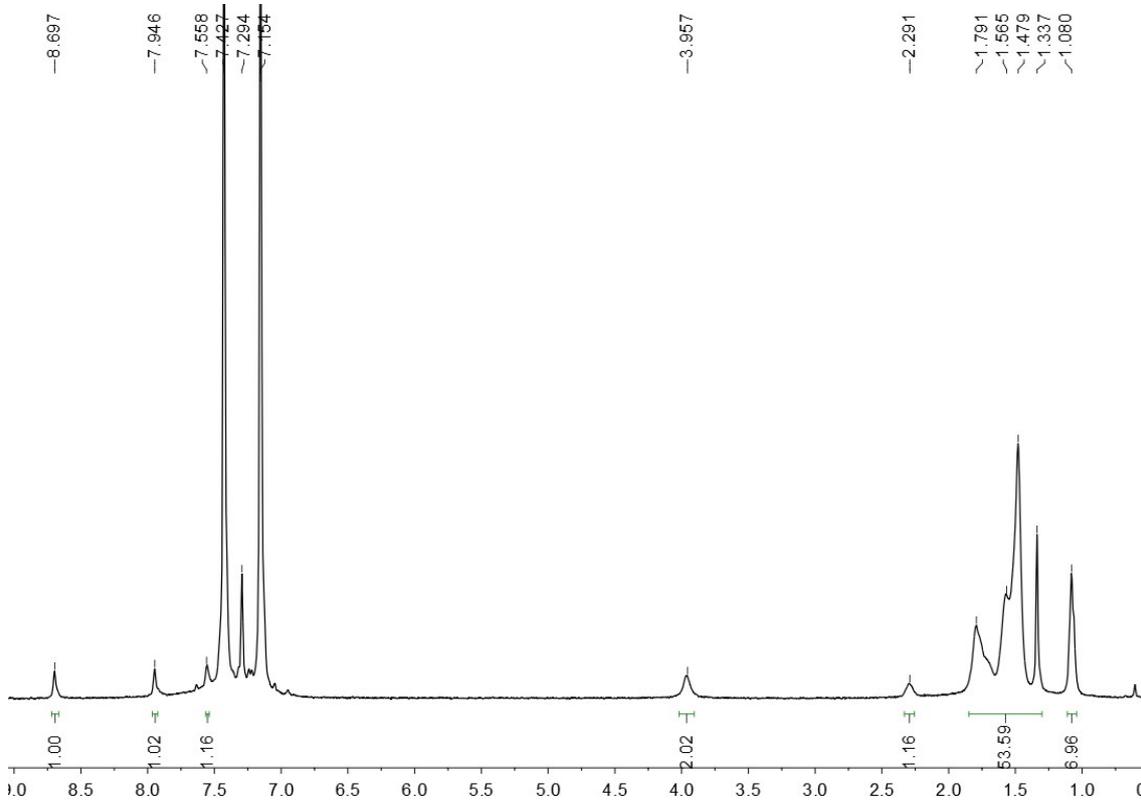
Figure S20. ^{1}H NMR spectrum of **P-BNBP-BT**.

17
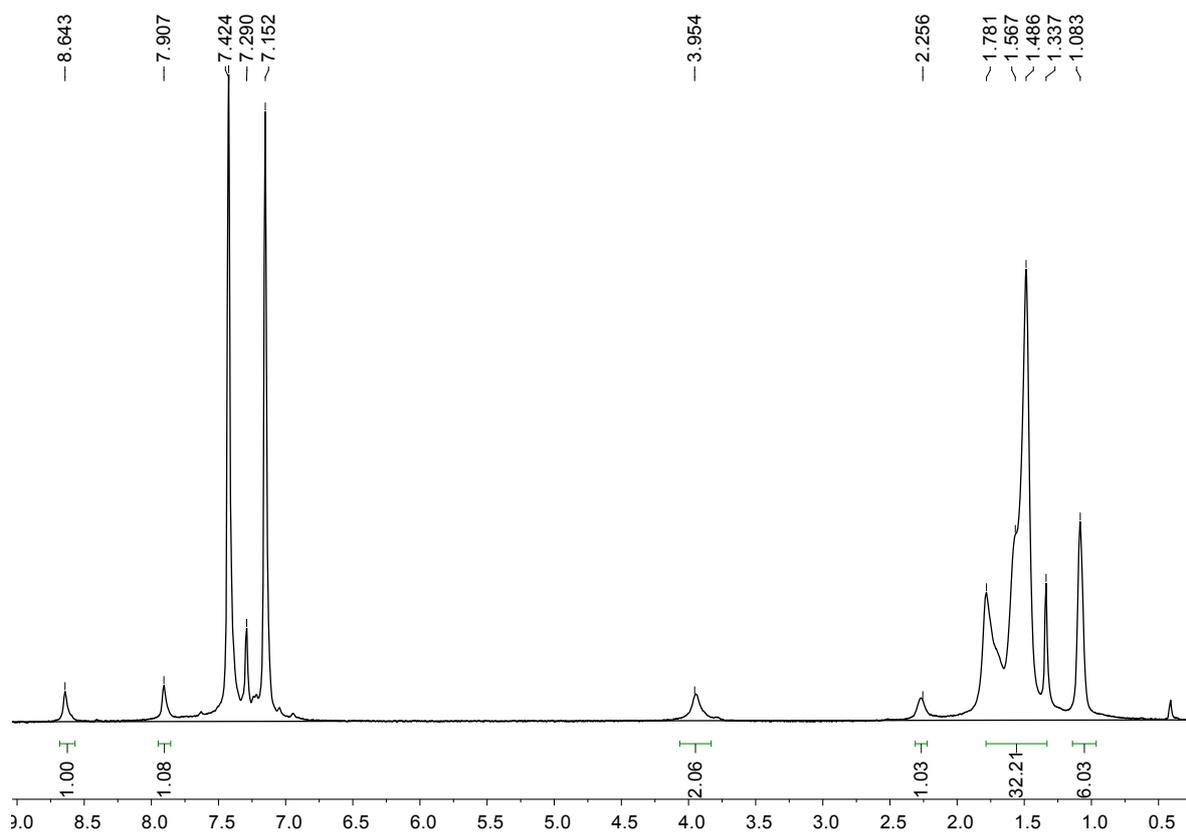
Figure S21. ^{1}H NMR spectrum of **P-BNBP-fBT**.